

Autonomous In-situ Analysis of the Upper Ocean: Construction of a Compact, Long Pathlength Absorbance Spectrometer.

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LONG-TERM GOALS

Our research is directed toward utilization of modern optoelectronic technology for real-time monitoring of the ocean's chemical environment with a subtlety and sophistication equivalent to senses of taste and smell. We have made significant advances toward real-time observation of chemical signals with sensitivities comparable to those of the ocean's natural inhabitants.

OBJECTIVES

The broad objective of this work is the development of a miniature, long pathlength spectrophotometer for *in-situ* elemental analysis. The long pathlength of this spectrometer (5 meters) extends the limits of detection of conventional spectrophotometric analyses by close to two orders of magnitude. Realization of our objectives is being pursued through system miniaturization to an extent that will allow construction, in a small volume, of a multiple-spectrometer system capable of rapid, simultaneous analysis of a variety of solutes.

APPROACH

This proposal is specifically directed to the design and construction of a Spectrophotometric Elemental Analysis System (SEAS-1) which will provide an integrated view of the ocean's chemical environment. The underlying design approach behind SEAS-1 is the development of a miniature, inexpensive instrument which is easily reconfigurable to measure a wide variety of solutes. Liquid Core Waveguides (LCW) provide a simple and powerful means of implementing long pathlength absorbance spectroscopy (LPAS). The methods outlined in this work can be used to extend the spectrophotometric detection limits of many chemical species.

Key personnel: EA Kaltenbacher (Lead Engineer), RH Byrne (Lead Scientist), W Yao (Post Doctoral Research Associate) and Center for Ocean Technology Engineers.

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WORK COMPLETED

The initial phase of this project focused on the development of a miniature long pathlength optical cell. An LCW was chosen for this work after investigation of several alternative optical designs. LCW's provide for long optical pathlengths by constraining light propagation within a liquid medium which has a higher refractive index (R.I.) than the surrounding tubing. While LCW's have been around for many years (Stone, 1972), they have all been confined to liquids with higher refractive indices than that of water (R.I. ~ 1.33). A material search uncovered an Amorphous Fluoropolymer form of Teflon designated AF-2400 which has an R.I. of ~ 1.29 . An LCW constructed of Teflon AF-2400 with a water core provides total internal reflection for light rays intersecting the water/tubing interface at 19° or less.

We have developed a Liquid Core Waveguide system with many highly desirable properties (i.e. miniature, chemically inert, flexible, low insertion loss, low sample volume, easily manufactured and maintained, etc.). Our spectrophotometric procedures provide the Fe(II), Cr(VI) and NO_2^- concentration versus absorbance responses shown in Figures 1 and 2 (Waterbury et al, 1997; Yao et al, 1998; Yao and Byrne, in-press). The detection sensitivities for all investigated chemical species are nanomolar to sub nanomolar. Our procedures can be extended to pH and alkalinity analysis as well as many other chemical species.

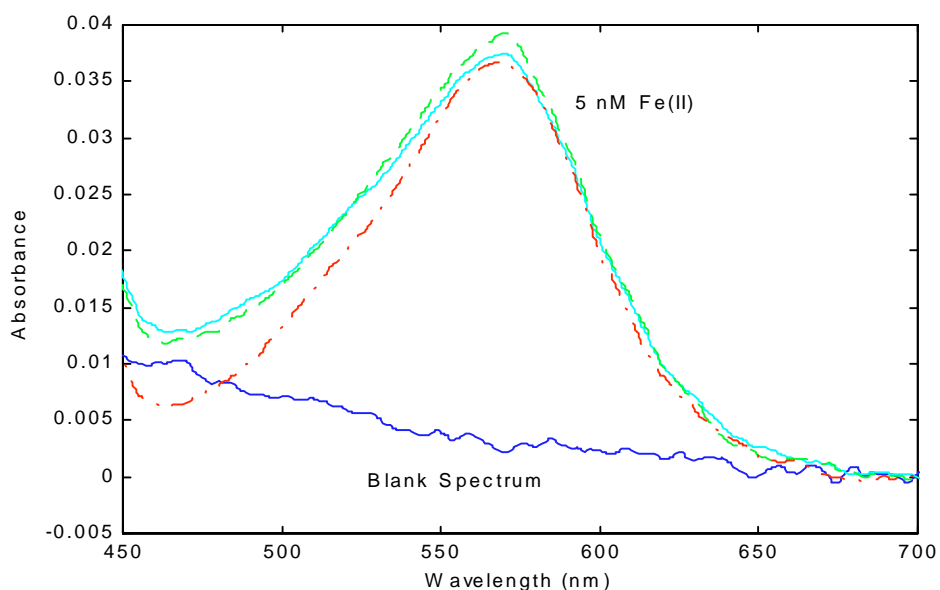
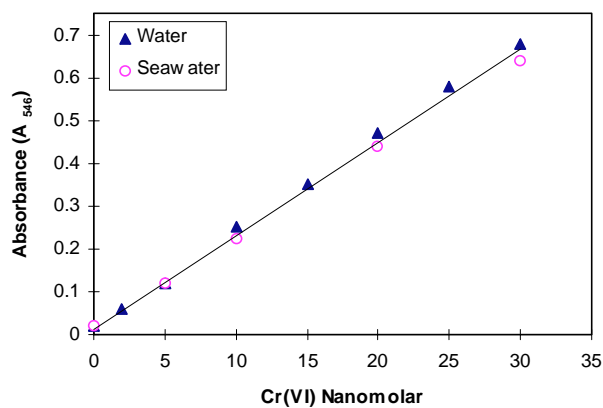
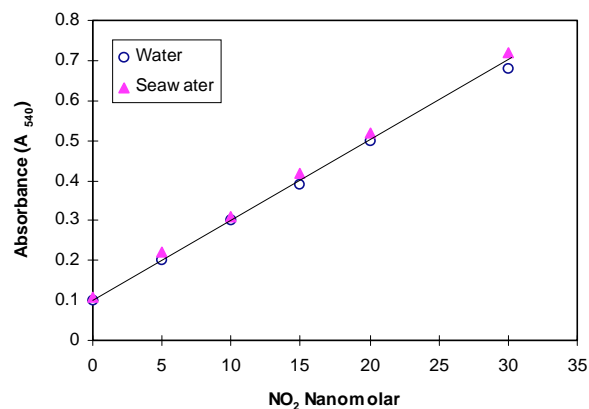


Figure 1: Three replicate measurements of a 5nM Fe(II) sample using a 2.75 meter long LCW. Also shown in the figure is a blank spectrum consisting of water + buffer + Ferrozine.



(a)



(b)

Figure 2: (a) Chromate (CrO_4^{2-}) standard curves (0-30nM) for Milli-Q water and seawater obtained using a 5.0m LPAS system, (b) Nitrite (NO_2^-) standard curves (0-30nM) for Milli-Q water and seawater obtained using a 4.5m LPAS system.

The first prototype of the SEAS instrument was completed in early 1998. This instrument is shown in Figure 3. It is capable of autonomous operation down to a depth of 500 meters. The miniaturized spectrometer used as the detector in the system allows analysis of spectrophotometric response over a wide range of wavelengths. The instrument is operated by an on-board micro-processor which controls all functions including pump rates of liquids, data acquisition, start and stop, and data storage and transmission. Software has been optimized for 2048 element spectral acquisition in 21ms (100KHz A/D rate) with an absorbance precision of 0.001 AU.



Figure 3: A photo of the SEAS instrument. The instrument is 18 inches long and has a diameter of 4.5 inches.

Our LPAS systems have been transitioned from the laboratory to systems capable of autonomous in-situ analysis. Circuit boards were designed and manufactured for a small overall volume and low power consumption. Our in-situ system is 4.5 inches in diameter, 18 inches long and weighs roughly 6 pounds. A new method for coupling light into the LCW was designed. This new coupling allows for reduced data collection times, as well as improved liquid flow rates through the LCW. Most importantly, shorter collection times provide measurements with an increased signal to noise ratio. In conjunction with the improved light coupling, an industry search was performed to provide a light source with optimal intensity, spectral content, and physical size for the instrument. Light-source improvements in conjunction with the improved light coupling produced a 25 fold reduction in data acquisition time. We are in the process of building two instruments for deployment in late 1998. These two instruments will allow measurement of several different chemical species and will facilitate the transitioning of this technology to industry.

RESULTS

In this project we pursued an ambitious goal: development of a one meter pathlength absorbance spectrometer. It was noted that achievement of this goal would extend the limits of detection of conventional spectrophotometric analysis by at least an order of magnitude. Through development of 5 to 10 meter pathlength systems for analysis of dissolved chemical analytes we have considerably exceeded our design goal. Using our LPAS systems and colorimetric procedures for seawater analysis developed by many investigators over more than fifty years, the chemistry of the upper ocean can be studied in a manner heretofore impossible. With a single type of measurement, long pathlength absorbance spectroscopy, simultaneous in-situ analysis for a wide variety of solutes can be obtained rapidly and without preconcentration.

A Liquid Core Waveguide has been discovered and characterized for use as a miniature, multi-meter optical path. The key advantages of this LCW in LPAS analyses are:

1. Sub-nanomolar detection sensitivity
2. Adjustable sensitivity by varying the waveguide length
3. Long pathlengths (e.g. 5m) can be coiled within extremely small volumes ($\approx 10 \text{ cm}^3$)

A prototype SEAS instrument has been constructed and tested in the laboratory. Redesign of the system, involving circuit board reconfigurations and optical design improvement is in progress. Field testing of the redesigned SEAS instrument will begin in December of 1998.

IMPACT/APPLICATIONS

The LPAS technology presented in this work can be used to markedly extend the detection capabilities of many existing solution-based measurements obtained via absorbance spectroscopy. Applications of this technology will include both seawater and freshwater (rivers, lakes, subterranean waters, and drinking water (Yao and Byrne, in press). The analytical apparatus required for this analysis is extremely sensitive, very simple and

inexpensive. Our LCW experimental setup is ~\$10K less expensive than conventional spectrophotometry and yet is orders of magnitude more sensitive.

TRANSITIONS

The technology developed in this project is being used as a basis for research funded by the National Oceanic Partnership Program (NOPP BAA/ONR32) supported by the Office of Naval Research under Award No. N00014-98-1-0803 with the University of South Florida as a subcontractor to the Regents of the University of Southern California. In this project oceanographic systems (including SEAS instruments) are being configured for long-term autonomous operations on deep-sea moorings.

RELATED PROJECTS

Sensor development costs are being shared between this project and L. Garcia-Rubio's project titled "Spectroscopy Characterization of Micron and Sub-micron Marine Particles" within a portion of T. Hopkins' program titled "Comprehensive Marine Particle Analysis System". Due to design similarities between these two sensors it is possible to combine development costs and maximize funding resources.

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